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(54) Peroxide preparation

(57) Mixtures containing different ketone peroxides are prepared by peroxidizing one or more ketones in an organic solvent medium containing at

least one preformed peroxide of a different ketone. The process can be effected as a reaction sequence and is particularly useful in those cases where the ketones, for efficient peroxidation with hydrogen peroxide, require different pH conditions.

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SPECIFICATION

Improvements in and relating to peroxides

The present invention concerns a process for the preparation of ketone peroxide mixtures, such as are particularly useful as polymerization initiators for unsaturated polyester resins.

5 It is known (Modern Plastics, January 1962 p. 135—163) that some organic peroxides, when used as polymerization initiators for unsaturated polyester resins, interact with each other causing unexpected effects. In fact, numerous catalytic systems comprising two or more peroxides may display a synergistic activity.

10 Although catalytic systems having only one peroxide are generally satisfactory, resort may be had to catalytic systems having more peroxides in particular cases, such as for instance when long pot life is required of the unsaturated polyester resin incorporating peroxide only, at room temperature, associated with fastgel and hardening times or with long gel times associated with fast hardening times.

For this purpose, in general there are used in practice combinations of standard commercial formulations of individual organic peroxides, added separately to the unsaturated polyester resin at the time of use.

15 Moreover, it is possible to use for the above-said purpose mixtures of separately preformed peroxides which are mutually compatible and form mixtures that have good storage stability and are safe in handling.

20 In particular, in the case of the ketone peroxides, for which the foregoing is also valid, it is known to be possible to obtain mixtures directly by carrying out the peroxidation with hydrogen peroxide of two or more ketones simultaneously, in the presence or absence of desensitizing diluents, using catalysts such as inorganic or organic acids, cationic resins or mineral clays (USP 3,015,631).

25 These methods of mixed synthesis have, however, the limitation in that they can be carried out only with ketones that require a very similar concentration of hydrogen ions for the peroxidation reaction with hydrogen peroxide.

A process has now been found which will allow mixtures based on ketone peroxides to be prepared, from ketones which need different concentrations of hydrogen ions for the peroxidation reaction, and which could not readily be obtained by physically mixing together two or more preformed formulations, if only because of the instability and hazardous nature of one or more of the components of the desired mixtures.

30 According to the invention, a process for the preparation of mixtures containing different ketone peroxides comprises effecting peroxidation of one or more ketones in an organic solvent medium containing at least one preformed peroxide of a different ketone.

35 Suitably from 0.01 to 0.7 mols. of ketone to be peroxidised, and 0.03 to 1.5 mols of hydrogen peroxide are used in 100 g of reaction mixture at 0—50°C for 5 minutes to 16 hours, optionally in the presence of a desensitizing diluent.

40 An important feature of the invention is that the preformed peroxide may be prepared at an appropriate pH by reaction of the different ketone or ketones, and the product may then, by adjustment of the pH, be used as medium for the preparation of peroxides of other ketones at a different appropriate pH. In particular it is found convenient to use for the preformed peroxides, a ketone or ketones requiring a relatively low pH for optimum conversion to peroxide (generally by treatment with hydrogen peroxide). The ketone or ketones to be peroxidised may then be treated with hydrogen peroxide at an appropriate, higher pH in the presence of the preformed peroxide.

45 It will be understood that the preparation of the preformed ketone peroxide may precede the peroxidation of the other ketone or ketones in a sequential reaction, with pH adjustment between the peroxidation stages of the respective ketones; or the preformed ketone peroxide may be procured from other sources for example as a commercial preparation.

In the case of a sequential reaction the pH may be adjusted for instance by addition of alkali or by mechanical elimination of an acidic solid reaction catalyst.

50 In the final formulation, the ketone or ketones may be either partially or totally peroxidized and some or no residual hydrogen peroxide may be present.

Examples of ketones that may be used for the first peroxidation stage, that is, for the preparation of the preformed peroxide, are: methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, methyl cyclohexanone, 3,3,5-trimethyl cyclohexanone, and the like, and mixtures thereof.

55 Examples of ketones that may be used for the second stage of the peroxidation, i.e. in the presence of preformed ketone peroxide, are: 1,3-diketones (such as acetylacetone), 1,4-diketones (such as acetonylacetone), alpha, beta or gamma hydroxyketones (such as diacetone alcohol), and alpha, beta or gamma alkoxyketones (such as 4-methoxy-4-methyl-pentan-2-one), and the like, and their mixtures.

60 The hydrogen peroxide used in the process suitably has a concentration comprised between 35—85% by weight, preferably between 50 and 70%.

The peroxidation reaction of the second stage may be conducted by adding the total required quantity of hydrogen peroxide in the second stage, but may also be carried out in the case of sequential reaction by introducing some or all of the required hydrogen peroxide in the first stage, i.e. when the preformed ketone peroxide is being prepared. Further, it is possible to utilise any unreacted hydrogen

peroxide, which is often present in standard formulations based on ketone peroxides (such as commercial methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide, cyclohexanone peroxide, and the like), in order to carry out the peroxidation of suitable quantities of the ketones usable for the second peroxidation stage. This residual hydrogen peroxide may of course be supplemented as required. In that second stage there may optionally be added one or more suitable diluents serving to attenuate the product and thus afford an active oxygen content such as will provide safety in the utilization of the product, as well as stability during storage.

Where the preformed ketone peroxide formulation already incorporates sufficient desensitizing diluent, the second stage of the peroxidation may be conducted without any further addition of such diluent.

The solution of preformed ketone peroxide, suitably obtained from a first peroxidation stage, representing the reaction medium, desirably constitutes from 5 to 95 g per 100 g of reaction mixture. As already indicated, hydrogen peroxide is desirably present in an amount of from 0.03 to 1.5 mols in 100 g of reaction mixture, and the ketone or ketones to be either totally or partially peroxidized should be present in an amount of from 0.01 to 0.7 mols in 100 g of reaction mixture. Any desensitizing diluent suitable for diluting the reaction mixture is desirably used in an amount of from 0 to 50 g in 100 g of reaction mixture.

As is well known, peroxides in general manifest a potential for violent decomposition by way both of detonation and of conflagration, and they also in varying degrees undergo progressive self-decomposition under storage conditions resulting in poor shelf life. These tendencies can be attenuated by dilution, but by no means all solvents are suitable for this purpose. Some, such as acetone, themselves can react with hydrogen peroxide to form even more hazardous peroxides apart from reducing the flash point; others, although decreasing the potential for violent decomposition, actually increase the self-destruction rate under storage conditions. Suitable diluents are known in the art as desensitizing solvents or desensitizing diluents, sometimes referred to as "phlegmatizers". In the following description and claims, references to diluents will be understood to be to such desensitizing diluents or phlegmatizers. Suitable diluents include phthalic esters, phosphoric esters, glycols, ether-glycols, alcohols and the like; while the preferred diluents are triethyl phosphate, dimethyl phthalate and dipropylene glycol. Desirably the chosen diluent is compatible with unsaturated polyester resins.

The peroxidation temperature is preferably maintained at 10° to 35°C while the reaction time is suitably from 5 minutes to 8 hours.

The resulting mixture of ketone peroxides may have an active oxygen content of 3% to 12%, preferably 5% to 10%.

Preferred mixtures that may be prepared according to this invention are based on: methyl ethyl ketone peroxide — acetylacetone peroxide, methyl isobutyl ketone peroxide — acetylacetone peroxide, methyl ethyl ketone peroxide — diacetonealcohol peroxide, and on cyclohexanone peroxide and methyl cyclohexanone peroxide — acetylacetone peroxide.

From such mixtures it is possible to prepare an unlimited number of formulations by varying suitably the quantities of the reactants used in the second stage of peroxidation: in this way it is possible to satisfy the requirements of a much wider field of industrial applications.

Mixtures of two or more ketone peroxides prepared according to the invention possess considerable cross-linking activity when used as polymerization initiators for unsaturated polyester resins, not always matched by adding separately to the resin the individual components of the mixture.

That the process of the invention actually achieves the formation of ketone peroxides in the second peroxidation stage with hydrogen peroxide, and the mixtures thus formed consist of ketone peroxides and not of unreacted mixtures of ketones with H_2O_2 , is supported by N.M.R. analysis to which the mixtures prepared in the following Examples 1—6 and in Preparation 4, had been subjected to establish the presence of 3,5-dimethyl-dihydroxy-1,2-peroxy-cyclopentane (acetylacetone peroxide) in the mixtures themselves.

In the following Table the chemical shifts found in all the examined mixtures are set out, as well as their attribution, with reference to the report in J.A.C.S. 1963 85 pages 222—225, by Milas Golubovic et al. Acetylacetone peroxide was signalled in all the above-indicated Examples and Preparation.

	Group	Chemical Shift	Atoms of H
ACETYLACETONE (2, 4-Pentane-dione) ketonic form: $\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \\ \parallel \quad \quad \parallel \\ \text{O} \quad \quad \text{O} \end{array}$			
enolic or related form: $\begin{array}{c} \text{CH}_3-\text{C}=\text{CH}-\text{C}-\text{CH}_3 \\ \mid \quad \quad \parallel \\ \text{OH} \quad \quad \text{O} \end{array}$	$\overline{\text{CH}_3}$	2.07	3
	$\overline{\text{CH}_2}$	3.70	2
	$\overline{\text{CH}_3}$	2.20	3
	$\overline{\text{CH}}$	5.66	1
ACETYLACETONE PEROXIDE (3,5-dimethyl-3,5-dihydroxy-1,2-peroxycyclopentane) $\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_2 \quad \quad \text{OH} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{C} \quad \quad \text{C} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{HO} \quad \quad \text{O}-\text{O} \quad \quad \text{CH}_3 \end{array}$			
Tetramethylsilane was used as reference compound.	$\overline{\text{CH}_3}$	1.50	3
	$\overline{\text{CH}_2}$	2.50	2
		2.58	2

The following series of Preparation and Examples illustrate how the invention may be carried into effect, without limiting the wider aspects thereof.

PREPARATION 1

5 A mixture of 33.7 g of 70% w/w H_2O_2 and 5.7 g of 2% w/w H_2SO_4 was added whilst stirring to a mixture of 23.2 g of methyl ethyl ketone (butane-2-one) and 26.8 g of dimethyl phthalate, in the course of about 30 minutes. The reaction mixture was cooled externally with water in order to prevent the temperature exceeding 35°C ; and then the mixture was stirred for a further 2 hours at 30°C .

10 The reaction mixture was then treated with an aqueous solution of NaOH (0.15 N) in such an amount as to allow the pH to settle between 4.0 and 4.5.

The liquid phases thus obtained were then separated and the organic phase, containing dimethyl phthalate and reaction product, was washed with an aqueous solution saturated with ammonium sulfate and then dried over anhydrous sodium sulphate.

15 There were thus obtained 67.7 g of methyl ethyl ketone peroxide solution containing 12.3% of active oxygen. To this solution were added 24.8 g of dimethylphthalate diluent, to yield 92.5 g of a ketone peroxide (MEKP) formulation in dimethylphthalate containing 9.0% active oxygen and having a final pH of about 4.5.

20 This formulation may be conveniently used either as a polymerization initiator for unsaturated polyester resins with a gel time of 14 minutes and a hardening time of 29 minutes, or as a solvent medium for carrying out the peroxidation of other ketones with hydrogen peroxide in accordance with the invention.

PREPARATION 2

A mixture, consisting of 31.93 g of 85% w/w H_2O_2 and 15.1 g of 12% w/w H_2SO_4 was added, whilst stirring, to a mixture of 39.84 g of methyl isobutyl ketone (4-methyl-pentane-2-one) and 39.21 g of dimethyl phthalate, over a period of about 45 minutes. The reaction mixture was kept cool externally by means of water, in order to avoid the temperature exceeding 30°C. The organic phase thus obtained was then separated from the aqueous phase and the organic solution containing methyl isobutyl ketone peroxide was treated with an aqueous solution of 0.2 N sodium hydroxide in such a quantity so as to bring the pH to 4.0—4.5.

The organic solution was then washed with a saturated aqueous solution of ammonium sulphate and dried over anhydrous sodium sulphate.

There were obtained 98.3 g of a ketone peroxide formulation based on methyl isobutyl ketone peroxide and containing about 10.1% of active oxygen, with a pH of about 4.5.

This formulation may be conveniently used as a polymerization initiator for unsaturated polyester resins, having a gel time of 13.3 minutes and a hardening time of 28 minutes, or may be used as a solvent medium for carrying out the peroxidation of further ketones with hydrogen peroxide in accordance with the invention.

PREPARATION 3

A commercially available formulation based on acetylacetoneperoxide (AAP) suitable for use as a polymerization initiator for unsaturated polyester resins was found to contain, in proportions by weight:

20	3,5-dimethyl-3,5-dihydroxyl-1,2-peroxycyclopentane	33.5%	20
	water	6.5%	
	triethylphosphate	60.0%	
	active oxygen	4.06%	
25	gel time	13 min	25
	hardening time	19 min	

This formulation is physically mixed together with the MEKP formulation, prepared as in Preparation 1, in order to carry out a comparison between the cross-linking activity of the physical mixtures thus obtained with the cross-linking activity of the mixtures obtained by peroxidation in a sequential reaction according to this invention as exemplified hereinafter.

For this purpose, in the following Preparation 4, there is described the preparation of the formulation obtained by physically mixing together MEKP with AAP (acetylacetone peroxide), and in the following Examples 1 to 6 are described the preparation of the formulations obtained by peroxidation according to this invention.

35 PREPARATION 4

Formulations A, B, C and D were prepared by physical mixing with stirring times of 30 minutes at 25°C. Their compositions are set out in the following schedule.

COMPOSITION

Formulation	MEKP Formulation	AAP Formulation
	(Content, %)	(Content, %)
A	53.0	47.0
B	59.3	40.7
C	64.0	36.0
D	77.3	22.7
E	83.8	16.2
F	92.5	7.5

10 wherein the MEKP formulation was prepared according to Preparation 1, while the AAP formulation was prepared according to Preparation 3. 10

EXAMPLE 1

15 To 116.6 g of a MEKP formulation of 9.0% w/w active oxygen strength, prepared as described in Preparation 1, there were added, whilst stirring, 37.4 g of acetylacetone, during a period of about 30 minutes. The reaction mixture was cooled by external application of water in order to prevent the temperature from rising above 30°C, and it was then kept stirred for a further hour at room temperature. 15

20 At the end of this time, whilst still stirring, there were added 33.2 g of an aqueous solution of 60% w/w hydrogen peroxide over a period of about 45 minutes, again maintaining the temperature below 35°C. Stirring was then continued for a further 90 minutes at 30°C and finally 32.8 g of triethylphosphate were added to yield 220 g of a mixture based on MEKP and AAP, having an active oxygen content of 9% by weight. 20

EXAMPLE 2

25 To 154.2 g of a MEKP formulation having 9.0% w/w of active oxygen, prepared as described in Preparation 1, there were added whilst stirring 59.0 g of triethyl phosphate, whereupon the mixture was kept stirred for 10 minutes at room temperature. 25

At the end of this time there were added 10.1 g of acetylacetone in the course of 15 minutes, the reaction mixture being cooled so as to maintain a temperature not exceeding 30°C.

30 The reaction mixture was then kept stirred at room temperature for another 30 minutes, after which it was treated with 36.7 g of an aqueous 60% w/w solution of H₂O₂ in the course of 35 minutes, whilst maintaining the temperature below 30°C. 30

The reaction mixture was kept stirred for another hour at 30°C, to give 260 g of a MEKP/AAP mixture having an active oxygen content of 9.3%.

EXAMPLE 3

35 To 211.2 g of a MEKP formulation with 9.0% w/w of active oxygen, prepared as described in Preparation 1, there were added whilst stirring 8.9 g of an aqueous 60% w/w solution of H₂O₂ in the course of 20 minutes, cooling the reaction mixture to prevent the temperature from exceeding 25°C. 35

40 There were then added 21.8 g of triethylphosphate in the course of 15 minutes at room temperature, under conditions of constant stirring. Then there were added 88.1 g of acetylacetone in the course of 1 hour, keeping the reaction mixture cooled so that the temperature did not exceed 30°C. The reaction mixture was then kept stirred for a further 90 minutes, to give 330 g of a mixture based on MEKP and AAP with 6.5% w/w of active oxygen. 40

EXAMPLE 4

45 To 239.6 g of a MEKP formulation with 9.0% w/w of active oxygen, prepared as described in Preparation 1, there were added, with constant stirring 28.5 g of 50% w/w H₂O₂ in the course of 30 minutes; whilst cooling the reaction mixture in such a way to maintain a temperature not exceeding 30°C. 45

50 There were then added 14.0 g of acetylacetone in the course of 1 hour, whilst maintaining the temperature below 25°C by external cooling. The reaction mixture was kept stirred for another 2 hours at 25°C, and finally treated with 27.9 g of triethylphosphate over a period of 30 minutes at 25°C, to 50

giving 310 g of product. The MEKP/AAP mixture thus prepared had an active oxygen content of 9.1% w/w.

EXAMPLE 5

- To 192.7 g of a MEKP formulation of 9.0% w/w active oxygen strength, prepared as described in Preparation 1, there were added in the course of 30 minutes, whilst stirring and cooling 11.5 g of H_2O_2 of 70% w/w strength. The temperature was maintained at 20°C. The mixture was then treated with 15.0 g of dimethylphthalate over a period of 10 minutes at room temperature, after which, whilst still stirring, there were added 10.8 g of acetylacetone over a period of 30 minutes whilst maintaining the temperature at 35°C.
- The reaction mixture was kept stirred for a further 45 minutes at 35°C, after which it was cooled down, to give 230 g of a MEKP/AAP mixture containing 9.2% w/w of active oxygen.

EXAMPLE 6

- To 333 g of a MEKP formulation of 9.0% w/w active oxygen strength, prepared according to Preparation 1, and maintained stirred at 25°C, there were simultaneously, added, in the course of 30 minutes, 9.7 g of 60% w/w H_2O_2 and 17.3 g of acetylacetone.
- The reaction mixture was kept stirred at 25°C for a further hour, to give 360 g of a MEKP/AAP mixture having an active oxygen content of 8.5% w/w.

EXAMPLE 7

- The characterization of the cross-linking activity of the formulations described in Examples from 1—6, with the product of Preparation 4 as a control, was carried out using an unsaturated polyester resin of the following composition:

	phthalic anhydride	0.6 mols	} 65% by weight	
	maleic anhydride	0.4 mols		
	propylene glycol	1.0		
25	styrene monomer		35% by weight	25
	hydroquinone		130 p.p.m.	
	cobalt octoate (as Co^{2+})		90 p.p.m.	

The determinations were carried out in a bath stabilized at 20°C, on 50 g of activated resin with 2% w/w of each ketone peroxide formulation.

- The results of the cross-linking activity, expressed as gel and hardening times, obtained with the formulations described in Preparation 4 and Examples 1—6, are set out in the following Tables:

TABLE A			TABLE B			
Prepn. 4	Gel time mins.	Hardening time mins.	Example No.	% MEKP	Gel time mins.	Hardening time mins.
A	15.6	23.6	1	53.0	12.3	19.5
B	15.9	24.3	2	59.3	10.1	19.0
C	15.7	24.8	3	64.0	15.0	23.4
D	15.1	26.3	4	77.3	12.6	22.4
E	14.8	27.0	5	83.8	13.6	24.2
F	14.4	28.1	6	92.5	24.0	37.0

These results are from formulations having a MEKP content (at 9% w/w of active oxygen) of 53% to 92.5%.

- For the formulation of Preparation 4 (Table A) the gel times were from 14.4 to 15.9 minutes, whilst the hardening times were from 23.6 to 28.1 minutes.

For the formulations of Examples 1—6 (Table B) the gel times were from 10.1 to 24 minutes, while the hardening times were from 19 to 37 minutes.

The peroxide formulations according to the invention therefore provide for wider ranges of gel and hardening times inasmuch as the quantity of reactants participating to the second peroxidizing stage can be varied continuously: in this way a practically unlimited number of formulations having an equal MEKP content are made available and thus the possibilities of industrial application are considerably expanded.

The following Table C lists the cross-linking activities, expressed in gel and hardening times, of 3 formulations in which the quantities of acetylacetone are varied and the quantities of methyl ethyl ketone peroxide and hydrogen peroxide are maintained constant in order to obtain formulations having the same active oxygen content, the MEKP content being 75% in each case.

TABLE C

Peroxide Test	Cross-linking activity	
	Gel Time	Hardening Time
	minutes	minutes
a	18.7	29.3
b	13.7	26.7
c	16.0	29.5

TEST a

To 150 g of a MEKP formulation of 9.0% w/w active oxygen strength, prepared as described in Preparation 1, there were added with constant stirring 10.4 g of 60% w/w H_2O_2 over a period of 30 minutes, cooling the reaction mixture externally so that the temperature did not exceed 30°C.

Thereupon there were added 16.8 g of acetylacetone over a period of 1 hour, maintaining the temperature below 25°C by external cooling.

The reaction mixture was then kept stirred for another 2 hours at 25°C and finally, over a period of 30 minutes and at 25°C, there were added 22.8 g of triethylphosphate. There were obtained 200 g of a MEKP/AAP mixture having an active oxygen content of 8.2% w/w.

TEST b

To 150 g of a MEKP formulation as in Test (a) there were added, whilst stirring, 10.4 g of 60% w/w H_2O_2 in the course of 30 minutes, the reaction mixture being cooled externally so that the temperature did not exceed 30°C.

Thereupon, to this reaction mixture there were added 4.2 g of acetylacetone over a period of one hour, whilst maintaining the temperature below 25°C by external cooling. This reaction mixture was then kept stirred for a further two hours at 25°C.

Finally there were added, in the course of 30 minutes, 35.4 g of triethylphosphate at 25°C, to give 200 g of a MEKP/AAP mixture containing 8.2% w/w of active oxygen.

TEST c

To 150 g of a MEKP formulation as in Test (a) there were added, whilst stirring, 10.4 g of 60% w/w H_2O_2 in the course of 30 minutes, the reaction mixture being cooled externally so as to prevent the temperature from exceeding 30°C.

Thereupon there were added 8.4 g of acetylacetone in the course of 1 hour, maintaining the temperature below 25°C by external cooling. The reaction mixture was kept stirred for another two hours at 25°C, and finally, there were added to it 31 g of triethylphosphate in the course of 30 minutes at 25°C to give 200 g of a MEKP/AAP mixture containing 8.2% w/w of active oxygen.

EXAMPLE 8

The cross-linking activity of the peroxid formulation of Example 3, in comparison with that of the unreacted components used in preparing the same, was determined by test polymerisations of an unsaturated polyester resin as described in Example 7.

The results, as set out in the following Table, show that the peroxidation method according to this invention actually effects peroxidation of the ketone in the second peroxidation stage.

TABLE

Formulation Used	Concentration on the Resin	Gel Time	Hardening Time
	% w/w	minutes	minutes
1) Mixture of Example 3	2	15.0	23.4
2) MEKP Preparation (1)	1.280	8.5	16.5
60% w/w H ₂ O ₂	0.054		
Acetylacetone	0.534		
Triethylphosphate	0.132		
Total:	2.000		

EXAMPLE 9

A methyl isobutyl ketone peroxide (MIBKP) formulation, with 10.0% w/w active oxygen, was used as reaction medium for the peroxidation of acetylacetone with hydrogen peroxide.

To 160 g of a MIBKP formulation containing about 10.0% w/w active oxygen, prepared as described in Preparation 2, there were added, under conditions of constant stirring and whilst maintaining the temperature below 30°C by external cooling, 20 g of acetylacetone over a period of 30 minutes.

This reaction mixture was then kept stirred for another 30 minutes, after which, in the course of 45 minutes, there were added 8.8 g of 60% w/w H₂O₂, maintaining the temperature below 35°C. The reaction mixture was then kept stirred for a further 45 minutes, after which it was treated with 28.6 g of triethylphosphate to give a mixture based on MIBKP and AAP containing 8.5% w/w of active oxygen.

The cross-linking activity of this catalyst was then determined with respect to the unsaturated polyester resin described in Example 7.

The results obtained were as follows: gel time 15.8 minutes; hardening time 24.8 minutes. The concentration of the MIBKP/AAP mixture used in the resin amounted to 2% by weight.

EXAMPLE 10

Diacetone alcohol was peroxidized with hydrogen peroxide, using as solvent medium a MEKP formulation.

To 320 g of a MEKP formulation with 9.0% w/w of active oxygen, prepared as described in Preparation 1, there were added, whilst stirring and maintaining the temperature below 25°C, and over a period of 20 minutes, 40 g of diacetone alcohol (4-methyl-4-hydroxy-pentane-2-one).

The reaction mixture was then kept stirred for another 40 minutes at 25°C and then, over a period of 30 minutes, there were added 17.6 g of 60% w/w H₂O₂ whilst maintaining the temperature below 30°C.

Stirring was continued for a further hour at 30°C, when there were added 22.4 g of triethylphosphate, to give 400 g of a mixture based on MEKP/Diacetone alcohol peroxide with an active oxygen content of 8.5% by weight.

The corresponding data on its cross-linking activity with the unsaturated polyester resin of example 7 are as follows: gel time 10.4 minutes; hardening time 23.4 minutes. The concentration of the catalyst MEKP/DAAP formulation in the resin amounted to 2% by weight.

EXAMPLE 11

The peroxidation of acetylacetone with hydrogen peroxide was carried out using as solvent medium a commercial mixture of cyclohexanone peroxide and methylcyclohexanone peroxide.

To 200 g of a commercial mixture of cyclohexanone peroxide and methylcyclohexanone peroxide there were added, whilst stirring and maintaining the temperature below 25°C, and over a period of 30 minutes, 50 g of acetylacetone (2,4-pentanedione).

The reaction mixture was then kept stirred for another 40 minutes at 25°C and then, during 1 hour there were added 57 g of 60% w/w H₂O₂, maintaining the temperature below 30°C. Stirring was continued for another hour at 30°C.

There were obtained 306 g of a mixture based on cyclohexanone peroxide, methylcyclohexanone peroxide and acetylacetone peroxide with an active oxygen content of 8.5% by weight.

The corresponding data on cross-linking activity with respect to the unsaturated polyester resin of example 7 are as follows: gel time 11.6 minutes; hardening time 23.9 minutes.

The concentration of the catalyst mixture in the resin was 2% by weight.

CLAIMS

1. A process for the preparation of mixtures containing different ketone peroxides which comprises effecting peroxidation of one or more ketones in an organic solvent medium containing at least one preformed peroxide of a different ketone.
- 5 2. A process according to claim 1, in which 0.01 to 0.7 mols of ketone to be peroxidised, and 0.03 to 1.5 mols of hydrogen peroxide are used in 100 g of reaction mixture at a temperature of 0°—50°C for a reaction time of 5 minutes to 16 hours, optionally in the presence of a diluent.
3. A process according to claim 1 or 2, in which a preformed organic solvent solution of said preformed peroxide constitutes from 5 to 95% by weight of the reaction mixture in which said peroxidation is effected.
- 10 4. A process according to claim 1, 2 or 3, in which said different ketone is selected from methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, methylcyclohexanone, 3,3,5-trimethylcyclohexanone and mixtures thereof.
5. A process according to any of claims 1 to 4, in which the ketone or ketones to be peroxidised is or are 1,3- or 1,4-diketones, alpha-, beta- or gamma-hydroxyketones or alpha-, beta- or gamma-alkoxy ketones or a mixture thereof.
- 15 6. A process according to claim 5 in which the diketone, hydroxyketone or alkoxyketone is selected from acetylacetone, acetonylacetone, diacetonealcohol and 4-methoxy-4-methyl-pentane-2-one.
- 20 7. A process according to any of the preceding claims in which the formation of the peroxide of said different ketone, and said peroxidation, are effected in sequence in first and second peroxidation stages by reaction of the respective ketone with hydrogen peroxide.
8. A process according to claim 7 in which the peroxidation stages are conducted at different pH levels, appropriate to the respective ketone or ketones undergoing peroxidation.
- 25 9. A process according to claim 8 in which the peroxidation of said different ketone or ketones is effected at a relatively low pH and the pH is then adjusted to a higher level for the second peroxidation stage.
10. A process according to any of the foregoing claims in which hydrogen peroxide used to effect peroxidation is added as an aqueous solution of 35—85% concentration by weight.
- 30 11. A process according to claim 10 in which said concentration is 50—70%.
12. A process according to any of the foregoing claims in which peroxidation is effected at 10—35°C for a period of 5 minutes to 8 hours.
13. A process according to any of the foregoing claims in which up to 50% by weight of the or each peroxidation reaction mixture is a diluent.
- 35 14. A process according to claim 13 in which the diluent is selected from triethyl phosphate, dimethyl phthalate and dipropylene glycol.
15. A process for preparing mixtures according to claim 1, substantially as described in any of the foregoing Examples.
16. Mixtures containing different ketone peroxides, when prepared as set forth in any of the foregoing claims.
- 40 17. Mixtures according to claim 16, in which the different peroxides comprise respectively methyl ethyl ketone peroxide — acetylacetone peroxide, methyl isobutyl ketone peroxide — acetylacetone peroxide, methyl ethyl ketone peroxide — diacetonealcohol peroxide, or cyclohexanone peroxide and methylcyclohexanone peroxide — acetylacetone peroxide.
- 45 18. Mixtures according to claim 16 or 17 in which the active oxygen content is in the range 5—10% by weight.
19. The use of mixtures according to claim 16, 17 or 18 as polymerization initiators for unsaturated polyester resins.